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Phase transformations in the synthesis of $La_{0.7}Sr_{0.3}MnO_3$ nanopowders

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$La_{0.7}Sr_{0.3}MnO_3$ nanopowder has been obtained by co-precipitation of the metal salts out of solution using sodium carbonate. The nanopowder synthesized contains two morphologically different particle types of 40 and 100 to 200 nm size. Using X-ray diffraction and transmission electron microscopy, phase transformations of the synthesis products have been studied within temperature range of 300 to 900°C. The nanoparticle formation genesis is traced and reasons for bimodal size distribution thereof are explained.

Нанопорошок $La_{0.7}Sr_{0.3}MnO_3$ получен методом совместного осаждения растворов солей металлов карбонатом натрия. Синтезированный нанопорошок состоит из двух типов частиц с размерами 40 и 100–200 нм и разной морфологической формой. Методами рентгеноструктурного анализа и просвечивающей электронной микроскопии исследовались фазовые превращения продуктов синтеза в интервале температур 300–900°C. Прослежен генезис образования наночастиц и объяснены причины их бимодального распределения по размерам.

Manganites $La_{1-x}M_xMnO_3$ (where M = Ca, Sr, Ba) take a specific place among oxides with the perovskite type ABO_3 structure. Numerous experimental and theoretical studies are aimed at those compounds [1–4]. Within a narrow composition range ($x = 1/3$), manganites exhibit strong ferromagnetic properties, a metal type conductivity, and a high sensitivity of electric conductance to external magnetic field (giant magnetoresistance). Those peculiarities appear due to a combination of different valence ions in crystallographically equivalent positions. To forecast new application fields of the manganites, it is necessary to understand clearly their physics where the structure, magnetic, and transport properties are interrelated.

It is lanthanum-strontium manganite $La_{0.7}Sr_{0.3}MnO_3$ that is of most interest for practical use, since it maintains its ferromagnetic properties at room temperature (T_c = 350 K). Today, there are already good prospects for production of cathodes for SOFC fuel elements and high-sensitive sensors on the basis of that material. To develop such devices, high-quality and stable materials with pre-specified properties are necessary, which cannot be obtained using the standard solid phase synthetic procedure. Development of oxide nanopowder technology is of a great interest in this connection. The transition to nanostructure state of a powder system makes it possible to attain a homogeneous chemical and phase composition and to provide the nanograin state of the ceramics. The latter fact is of a great importance for SOFC cathodes. The high specific surface of the porous cathode material enhances its catalytic activity as well as effective ionic conductance, since the distance that oxygen vacancies should overcome to the contact point with the electrolyte is reduced.

To obtain homogeneous and finely dispersed oxides, so-called "wet" chemical processes are used as a rule [5]. C.Vazques-Vazques et al. [6] have described the sol-gel

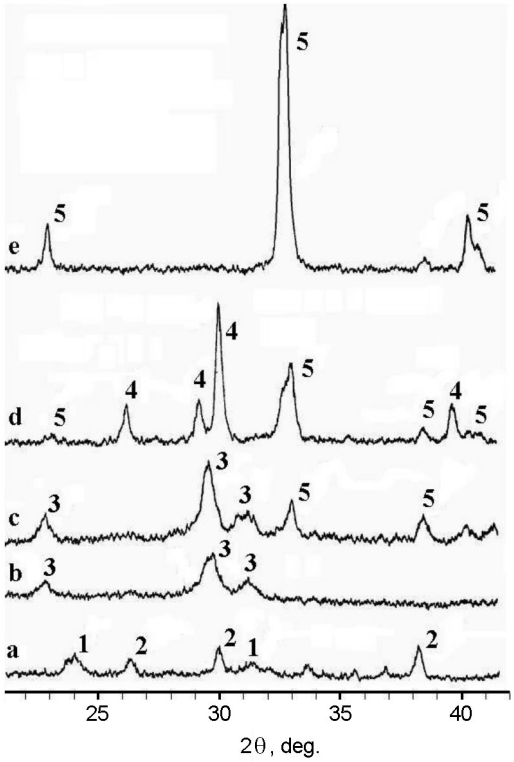

Fig. 1. XRD patterns from $La_{0.7}Sr_{0.3}MnO_3$ calcined at temperatures (°C): 300 (a), 400 (b), 600 (c), 700 (d), 850 (e). Reflections from phases are numbered as follows: $MnCO_3$ (*1*), $La_2O(CO_3)_2 \cdot xH_2O$ (*2*), La_2CO_5 (*3*), La_2O_3 (*4*), $La_{0.7}Sr_{0.3}MnO_3$ (*5*).

technology of $La_{0.7}Sr_{0.3}MnO_3$ production by evaporating the aqueous solution of cation nitrates. The samples obtained thereby at 800°C were of 60 nm size. R.F.C.Marques et al. [7] obtained $La_{0.7}Sr_{0.3}MnO_3$ of 200 nm particle size synthesized at 950°C without evaporation. These authors have used the co-precipitation of metal ions from salt solutions as insoluble hydroxides and/or oxocarbonates.

The co-precipitation method provides a homogeneous distribution of doping elements. The trend to agglomeration of the particles under subsequent heating does not allow to obtain the small primary particles, as is seen from [7]. To overcome this drawback, either a prolonged milling in various mills or spray drying at high or low temperatures is required. Our experimental investigations in preparation processes of ZrO_2 and TiO_2 nanopowders [8] have shown that a reduced extent of particle interaction following the co-precipitation and prevention of agglomeration at all the processing stages is attainable by pulse-wave actions,

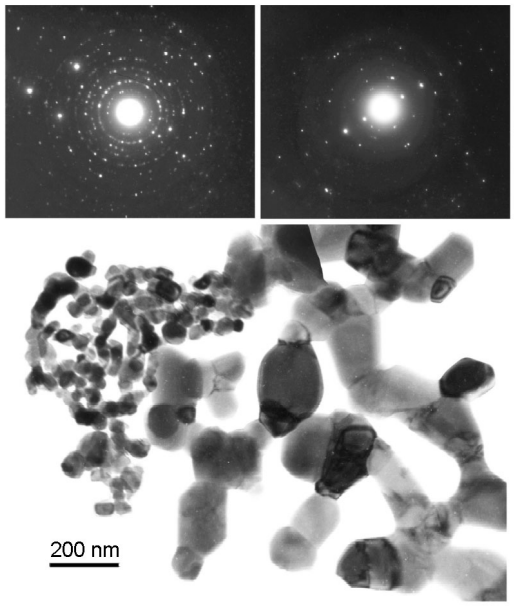

Fig. 2. Microstructure of $La_{0.7}Sr_{0.3}MnO_3$ nanopowder synthesized at 850°C.

namely, microwave heating, pulse magnetic field and ultrasonic treatment.

The $La_{0.7}Sr_{0.3}MnO_3$ samples were obtained by co-precipitation of metal salts from solution with sodium carbonate solution. Chemical purity grade La_2O_3, $MnCl_2 \cdot 4H_2O$, and $SrCl_2$ were taken as the initial materials in amounts corresponding to the desired product stoichiometry. Lanthanum oxide was dissolved in nitric acid. The mixing at room temperature for 1 h was used. The water-enriched precipitate of metal carbonates was washed in distilled water to remove the reaction by-products. The precipitate was dried at 110°C to constant weight and calcined at 300°C for 1 h. The lanthanum-strontium manganite precursor powder was treated by ultrasound to prevent the particle agglomeration. The $La_{0.7}Sr_{0.3}MnO_3$ phase composition was studied using X-ray diffraction (XRD) in Cu K_α radiation. Transmission electron microscopy (TEM) was used to study the morphology peculiarities of the phases involved in the synthesis. The samples of carbonates of all the metals contained in $La_{0.7}Sr_{0.3}MnO_3$ were prepared separately, maintaining the precipitation and synthesis conditions.

The lanthanum-strontium manganite precursor powder obtained by the co-precipitation undergoes a series of phase transformations in the course of $La_{0.7}Sr_{0.3}MnO_3$ synthesis. Fig. 1 presents X-ray photographs of samples obtained at different temperatures

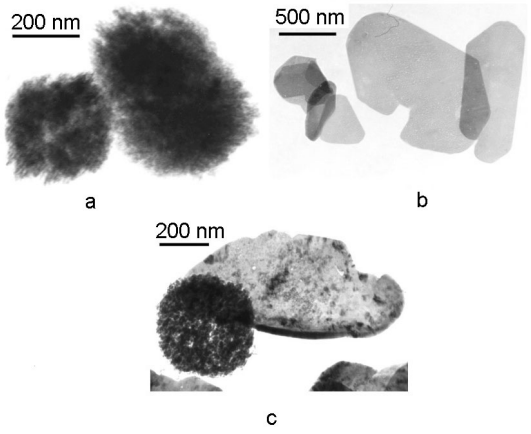

Fig. 3. Morphology of parent phases at different stages of $La_{0.7}Sr_{0.3}MnO_3$ synthesis: $MnCO_3$ (a) and $La_2O(CO_3)_2{\cdot}xH_2O$ (b) at 300°C; $La_{0.7}Sr_{0.3}MnO_3$ and La_2CO_5 at 500°C (c).

of sequential calcination. The washed, filtered, and dried mixture consists of amorphous metal carbonates. After calcination at 300°C, the powder x-ray pattern contains reflections from hydrocarbonate $La_2O(CO_3)_2{\cdot}xH_2O$ [11-PDF No.28-0512] and $MnCO_3$ (Fig. 1a). No strontium carbonate lines were found in the x-ray pattern within the XRD sensitivity. In the 300 to 400°C temperature range, dehydration takes place accompanied by partial decarbonization of the lanthanum component. The x-ray pattern taken at 400°C (Fig. 1b) shows reflections from the only La_2CO_5 phase. The absence of $MnCO_3$ lines is explained by the compound decomposition under decarbonization. The first signs of perovskite $La_{0.7}Sr_{0.3}MnO_3$ phase appears at 500°C. In the 500 to 700°C range, the amount of manganite increases under La_2CO_5 decrease (Fig. 1c). A CO_2 molecule release near 700°C results in La_2CO_5 transformation into lanthanum oxide La_2O_3 (Fig. 1d). At 700 to 850°C, the increase in manganite phase continues, but this time at the expense of into lanthanum oxide. According to our X-ray data, the formation of single-phase $La_{0.7}Sr_{0.3}MnO_3$ is over near to 850°C (Fig. 1e).

In the obtained $La_{0.7}Sr_{0.3}MnO_3$ powders, two morphologically different particle types were found by TEM studies. According to XRD and TEM, both types are identical in phase composition (Fig. 2). The first type is presented by small (40 nm) rounded particles accumulated in loose spherical aggregates. The second type includes large particles (100–200 nm) of polyhedral shape accumulated in porous polycrystals. The reason for the bimodal particle size distribution is made clear by structure studies of separately prepared metal carbonates and compounds obtained at different stages of $La_{0.7}Sr_{0.3}MnO_3$ synthesis. It is seen in Fig. 3 that manganese carbonate is shaped as spherical globules, while lanthanum carbonate, as flat crystals. The analysis shows that the initial carbonate shapes are inherited in the course of phase transformations. Fig. 4 illustrates the transformation path during $La_{0.7}Sr_{0.3}MnO_3$ preparation.

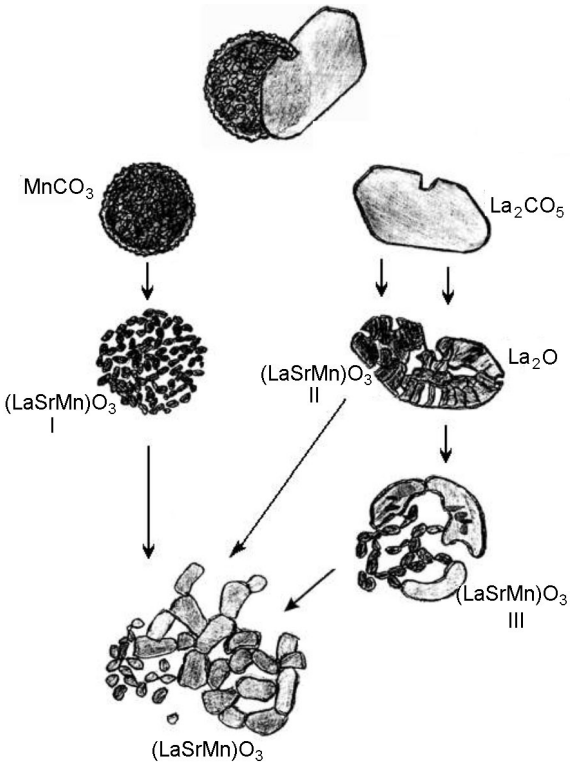

Fig. 4. Scheme of phase transformations in the course of $La_{0.7}Sr_{0.3}MnO_3$ synthesis.

The finely dispersed $La_{0.7}Sr_{0.3}MnO_3$ (Generation I) is formed after decomposition of $MnCO_3$ that is referred to as the first parent phase. It is just La_2CO_5 that becomes the second parent phase. Due to decomposition, it gives rise to two phases, La_2O_3 and $La_{0.7}Sr_{0.3}MnO_3$ (Generation II). As to La_2O_3 itself, it becomes later a parent and forms the third $La_{0.7}Sr_{0.3}MnO_3$ generation. The analysis of XRD patterns has shown that lanthanum oxide has somewhat enlarged unit cell parameters in this case. The increase of lattice parameters indicates that La ions in La_2O_3 are substituted in part by Mn and Sr ones. As the temperature attains

850°C, the final formation of single-phase $La_{0.7}Sr_{0.3}MnO_3$ takes place due to cation ordering. The Generations II and III are of the same dispersity. Thus, the bimodal distribution is due to formation of two particle types on the basis of manganese and lanthanum carbonates, respectively.

Thus, nanosized lanthanum-strontium manganite has been prepared using co-precipitation technique. Two observed particle types different in morphology and size are $La_{0.7}Sr_{0.3}MnO_3$ generations formed on the basis of two precursor phases (manganese and lanthanum carbonates). At 500°C, $MnCO_3$ undergoes dissociation, thus giving rise to the first (finely dispersed) manganite generation. Near 700°C, La_2CO_5 is decomposed forming two phases, La_2O_3 and the second (coarsely dispersed) $La_{0.7}Sr_{0.3}MnO_3$ generation. Next, the third (coarsely dispersed, too) $La_{0.7}Sr_{0.3}MnO_3$ generation is formed from La_2O_3. As a result, we have three generations of the same phase and two nanoparticle types of 40 and 100 to 200 nm size, respectively. A method is proposed to obtain nanosized $La_{0.7}Sr_{0.3}MnO_3$ with bimodal particle size distribution. Combining the small and large particle fractions in the nanopowders, it may be possible to improve the compacting results in the ceramics manufacturing. The understanding of decomposition processes and phase transformations in $La_{0.7}Sr_{0.3}MnO_3$ will result in improved techniques of manganite powders with pre-specified characteristics.

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Фазові перетворення під час синтезу нанопорошків $La_{0.7}Sr_{0.3}MnO_3$

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Нанопорошок $La_{0.7}Sr_{0.3}MnO_3$ одержано методом сумісного осадження розчинів солей металів карбонатом натрію. Синтезований нанопорошок складається з двох типів частинок із розмірами 40 та 100–200 нм і різною морфологією. Методами рентгеноструктурного аналізу і просвічуючої електронної мікроскопії досліджено фазові перетворення продуктів синтезу в інтервалі температур 300–900°C. Простежено генезис утворення наночастинок і пояснено причини їх бімодального розподілу за розмірами.